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NEWS 6	MAR 30	RDISCLOSURE reloaded with enhancements
NEWS 7	APR 02	JICST-EPLUS removed from database clusters and STN
NEWS 8	APR 30	GENBANK reloaded and enhanced with Genome Project ID field
NEWS 9	APR 30	CHEMCATS enhanced with 1.2 million new records
NEWS 10	APR 30	CA/CAplus enhanced with 1870-1889 U.S. patent records
NEWS 11	APR 30	INPADOC replaced by INPADOCDB on STN
NEWS 12	MAY 01	New CAS web site launched
NEWS 13	MAY 08	CA/CAplus Indian patent publication number format defined
NEWS 14	MAY 14	RDISCLOSURE on STN Easy enhanced with new search and display fields
NEWS 15	MAY 21	BIOSIS reloaded and enhanced with archival data
NEWS 16	MAY 21	TOXCENTER enhanced with BIOSIS reload
NEWS 17	MAY 21	CA/CAplus enhanced with additional kind codes for German patents
NEWS 18	MAY 22	CA/CAplus enhanced with IPC reclassification in Japanese patents
NEWS 19	JUN 27	CA/CAplus enhanced with pre-1967 CAS Registry Numbers
NEWS 20	JUN 29	STN Viewer now available
NEWS 21	JUN 29	STN Express, Version 8.2, now available
NEWS 22	JUL 02	LEMBASE coverage updated
NEWS 23	JUL 02	LMEDLINE coverage updated
NEWS 24	JUL 02	SCISEARCH enhanced with complete author names
NEWS 25	JUL 02	CHEMCATS accession numbers revised
NEWS 26	JUL 02	CA/CAplus enhanced with utility model patents from China
NEWS 27	JUL 16	CAplus enhanced with French and German abstracts
NEWS 28	JUL 18	CA/CAplus patent coverage enhanced

NEWS EXPRESS 29 JUNE 2007: CURRENT WINDOWS VERSION IS V8.2,
CURRENT MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP),
AND CURRENT DISCOVER FILE IS DATED 05 JULY 2007.

219-23°. The Et2O extract from IX was washed with aqueous NaHCO3 and H2O and treated 4 hrs. with aqueous Cu(OAc)2 to give 36% Cu chelate of β-phenylcinnamoylacetone (XII), m. 148-62°. The Et2O extract from X washed, dried, evaporated, and the residue treated with Cu(OAc)2 gave the Cu chelate of β-methylcinnamoylacetophenone (XIII), m. 206.6-8.5° (C6H6-alc.). A small sample of the Cu chelate of XIII was decomposed to give traces of XIII. The remainder of the oily residue from X triturated with ligroine gave 66% 2,3-dihydro-2,6-diphenyl-2-methyl-4H-pyran-4-one, m. 108-10° (hexane). Method B, with H2SO4. Samples (5 g.) of the hydroxy β-diones in 50 ml. cold concentrated H2SO4 were dissolved during 15 min., poured into ice H2O, and the products worked up as above. The product from VIII taken up in Et2O and the solution treated overnight with aqueous Cu(OAc)2 gave 58% Cu chelate of XI. Decomposition of this chelate with acid gave XI, m. 97-8°. After filtration of the Cu chelate of XI, the Et2O layer separated, washed with dilute acid, the solution dried, and the product recrystd. gave 15% 2,3-dihydro-2,2,6-triphenyl-4H-pyran-4-one (XIV), m. 145-8°. A better yield of XIV was obtained when the Cu(OAc)2 treatment was omitted.

If XIV were crystallized quickly from very concentrated MeOH it formed needles, m. 135° and 147-8°. The product from the dehydration of IX was similarly treated with Cu(OAc)2 to give 11% Cu chelate of XII, m. 161.5-3.0°. Decomposition of the Cu chelate with acid gave 72% XII, oil. The MeOH filtrate from the Cu chelate of XII, which had been recrystd., was diluted, acidified, and extracted with Et2O to give 21% 2,3-dihydro-2,2-diphenyl-6-methyl-4H-pyran-4-one (XV), m. 119-21°. A 48% yield of XV was obtained by evaporating the solvent from the Et2O solution of the dehydration product of IX and recrystg. β-Phenylcinnamic acid, prepared from 1,1-diphenylethylene and (COCl)2, was converted into its acid chloride with SOCl2. The acid chloride (6.5 g.) in 50 ml. Et2O added in the cold to 0.86 mole sodioacetophenone gave 41% III and 39% XI. XI (1 g.) in 10 ml. cold concentrated H2SO4 gave 0.28 g. XIV.

XIV (0.5 g.) in 10 ml. cold concentrated H2SO4 gave 50% recovery of XIV and treatment of th MeOH filtrate with Cu(OAc)2 gave 9% Cu chelate of XI.

Similarly, XII was converted into 29% XV and this product reconverted to XII as its Cu chelate in 18% yield. XIV (0.7 g.) refluxed 17 hrs. in 15ml

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                                                         ENTRY    SESSION
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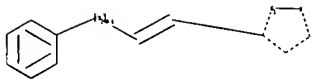

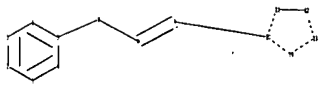

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7 8 9
ring nodes :
1 2 3 4 5 6 10 11 12 13 14
chain bonds :
5-7 7-8 8-9 9-10
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6 10-11 10-14 11-12 12-13 13-14
exact/norm bonds :
5-7 7-8 8-9 9-10 10-11 10-14 11-12 12-13 13-14
normalized bonds :
1-2 1-6 2-3 3-4 4-5 5-6
isolated ring systems :
containing 1 : 10 :

G1:O,S,N

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:CLASS 8:CLASS 9:CLASS
10:Atom 11:Atom 12:Atom 13:Atom 14:Atom

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L1      STRUCTURE UPLOADED

=> s l1
SAMPLE SEARCH INITIATED 14:17:47 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED -     2530 TO ITERATE

 79.1% PROCESSED     2000 ITERATIONS                          50 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS:  ONLINE  **COMPLETE**
                        BATCH   **COMPLETE**
PROJECTED ITERATIONS:        47583 TO    53617
PROJECTED ANSWERS:            3195 TO     4901

L2           50 SEA SSS SAM L1

=> s l1 ful
FULL SEARCH INITIATED 14:17:59 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -    50874 TO ITERATE

100.0% PROCESSED    50874 ITERATIONS                        4337 ANSWERS
SEARCH TIME: 00.00.01

L3         4337 SEA SSS FUL L1


=> file caplus
COST IN U.S. DOLLARS                          SINCE FILE      TOTAL
                                                 ENTRY    SESSION
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FILE LAST UPDATED: 19 Jul 2007  (20070719/ED)
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=> s l3
L6         1548 L3

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        2460806 PROCESS
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L7          890 L6 AND (PROCESS OR PREPAR? OR SYNTHES? OR METHOD OR MAKE OR
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         174289 ALCOHOLS
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        593237 ALC
        195275 ALCS
        692509 ALC
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        852081 ALCOHOL
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L8          62 L7 AND ALCOHOL

=> s l8 and base
        716911 BASE
        160082 BASES
        813421 BASE
                  (BASE OR BASES)
L9           8 L8 AND BASE

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L9   ANSWER 1 OF 8  CAPLUS  COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER:         2004:857573  CAPLUS
DOCUMENT NUMBER:          141:332188
TITLE:                    Process for preparation of
                          3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile
                          derivatives
INVENTOR(S):              Fukuda, Kenzo; Kondo, Yasuo; Tanaka, Norio; Suzuki,
                          Hideaki; Ohnari, Masatoshi; Nishio, Koichi
PATENT ASSIGNEE(S):       Nissan Chemical Industries Ltd., Japan
SOURCE:                   PCT Int. Appl., 41 pp.
                          CODEN: PIXXD2
DOCUMENT TYPE:            Patent
LANGUAGE:                 Japanese
FAMILY ACC. NUM. COUNT:   1
PATENT INFORMATION:

     PATENT NO.           KIND   DATE        APPLICATION NO.          DATE
     ---------------      ----   --------    --------------------     --------
     WO 2004087674         A1    20041014    WO 2004-JP4345           20040326
         W:  AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,
             CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,
             GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR,
             LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ,
             OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
             TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW
         RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ,
             BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE,
             ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
             SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,
             TD, TG
     BR 2004009529         A     20060418    BR 2004-9529             20040326
     CN 1768042            A     20060503    CN 2004-80008113         20040326
     JP 2004315513         A     20041111    JP 2004-95645            20040329
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US 2006178523	A1	20060810	US 2005-551041	20050927
PRIORITY APPLN. INFO.:			JP 2003-92029	A 20030328
			WO 2004-JP4345	W 20040326

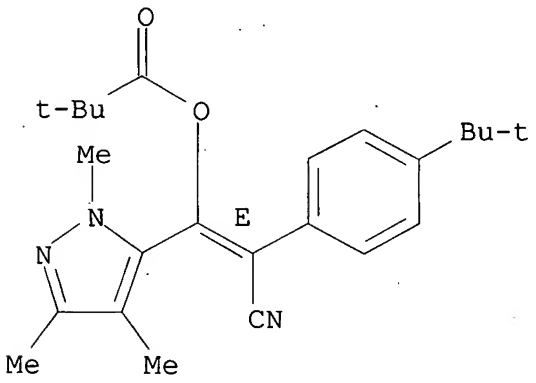
OTHER SOURCE(S): MARPAT 141:332188

IT 560121-52-0P
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(intermediate; preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)

RN 560121-52-0 CAPLUS

CN Propanoic acid, 2,2-dimethyl-, (1E)-2-cyano-2-[4-(1,1-dimethylethyl)phenyl]-1-(1,3,4-trimethyl-1H-pyrazol-5-yl)ethenyl ester (CA INDEX NAME)

Double bond geometry as shown.

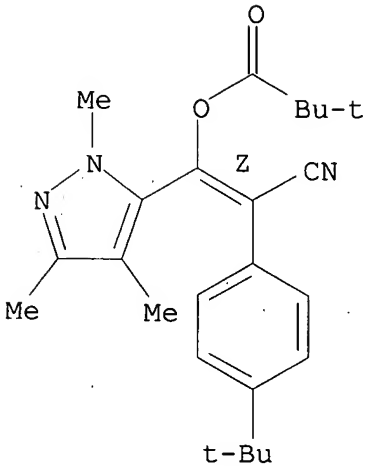


IT 560121-50-8P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)

RN 560121-50-8 CAPLUS

CN Propanoic acid, 2,2-dimethyl-, (1Z)-2-cyano-2-[4-(1,1-dimethylethyl)phenyl]-1-(1,3,4-trimethyl-1H-pyrazol-5-yl)ethenyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.



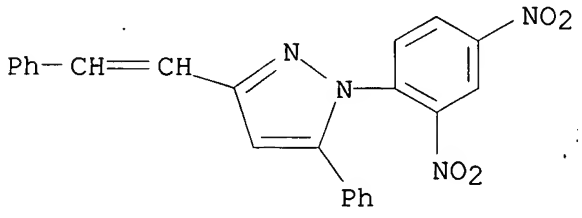
IC ICM C07D231-12
ICS C07D403-06
CC 28-8 (Heterocyclic Compounds (More Than One Hetero Atom))
Section cross-reference(s): 45
ST prepn pyrazolyl triazolyl acrylonitrile stereoselective
IT Acid halides
RL: RCT (Reactant); RACT (Reactant or reagent)
(acid chlorides; preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT Metal alkoxides
RL: RGT (Reagent); RACT (Reactant or reagent)
(alkali metal; preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT Alkali metal compounds
RL: RGT (Reagent); RACT (Reactant or reagent)
(alkoxides; preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT Esters, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(aromatic; preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT Isomerization
Polar solvents
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT Alcohols, preparation
RL: BYP (Byproduct); IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT Nitriles, preparation
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile

derivs.)
IT Hydrocarbons, uses
RL: NUU (Other use, unclassified); USES (Uses)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT Amines, reactions
RL: RGT (Reagent); RACT (Reactant or reagent)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT Coupling reaction
(stereoselective; preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT 379225-69-1P 560121-52-0P 773136-59-7P 773136-65-5P
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(intermediate; preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT 7647-01-0P, Hydrochloric acid, preparation
RL: BYP (Byproduct); IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT 379225-68-0P 560121-50-8P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT 104-90-5, 5-Ethyl-2-picoline 111-90-0, Diethyleneglycol monoethyl ether
111-96-6, Diethyleneglycol dimethyl ether 142-82-5, Heptane, uses
RL: NUU (Other use, unclassified); USES (Uses)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT 3282-30-2, Pivaloyl chloride 3288-99-1 89202-90-4 279682-51-8 773136-70-2
RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
IT 110-86-1, Pyridine, reactions 124-41-4, Sodium methoxide
RL: RGT (Reagent); RACT (Reactant or reagent)
(preparation of 3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile derivs.)
AB This invention pertains to a method for stereoselectively producing (E) or (Z) isomers of 3-acyloxyacrylonitrile derivs. Ar1C(CN)=C(Ar2)OCOR1 [wherein Ar1 and Ar2 = independently (un)substituted aryl; R1 = (un)substituted alkyl or aryl], which comprises reacting a 3-oxopropionitrile compound Ar1CH(CN)COAr2 with an acid chloride R1COCl, characterized in that the reaction is conducted with elimination of HCl or using a base to thereby regulate the stereostructure of the

reaction product; and a method of isomerizing the (E) isomer of the 3-acyloxyacrylonitrile compound into the (Z) isomer with an organic base. For example, 4-tert-butylphenylacetonitrile was reacted with 1,3,4-trimethylpyrazol-5-carboxylic acid Et ester in heptane and 5-ethyl-2-picoline in the presence of NaOMe to give 3-oxo-2-(4-tert-butylphenyl)-3-(1,3,4-trimethylpyrazol-5-yl)propionitrile (84.5%). The propionitrile obtained was reacted with pivaloyl chloride in xylene to provide (2E)-3-(2,2-dimethylpropanoyloxy)-2-(4-tert-butylphenyl)-3-(1,3,4-trimethylpyrazol-5-yl)acrylonitrile (91.9%). The (E) isomer of the acrylonitrile was treated with pyridine in MeCN to afford the (Z) isomer of the acrylonitrile in 99% purity. This invention provides a method to stereoselectively prepare acrylonitrile derivs. in high yield.

REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 2 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1974:107702 CAPLUS
DOCUMENT NUMBER: 80:107702
TITLE: Skipped diynes. V. Secondary diethynyl carbinols. Base-catalyzed ynol to enol rearrangements and ultraviolet spectra and conjugation
AUTHOR(S): Migliorese, Kenneth G.; Tanaka, Yoshinari; Miller, Sidney I.
CORPORATE SOURCE: Dep. Chem., Illinois Inst. Technol., Chicago, IL, USA
SOURCE: Journal of Organic Chemistry (1974), 39(6), 739-47
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
IT 50428-74-5P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
RN 50428-74-5 CAPLUS
CN 1H-Pyrazole, 1-(2,4-dinitrophenyl)-5-phenyl-3-(2-phenylethenyl)- (9CI) (CA INDEX NAME)

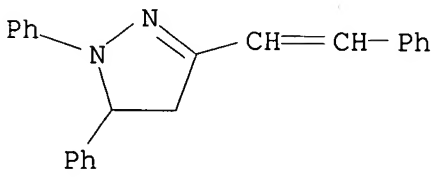


CC 22-6 (Physical Organic Chemistry)

IT 15814-32-1P 50428-54-1P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
(Reactant or reagent)
(preparation and reactions of)
IT 94-41-7P 27871-98-3P 37845-36-6P 50428-53-0P 50428-56-3P
50428-57-4P 50428-58-5P 50428-59-6P 50428-60-9P 50428-62-1P
50428-63-2P 50428-64-3P 50428-65-4P 50428-67-6P 50428-68-7P
50428-71-2P 50428-73-4P 50428-74-5P 50428-88-1P
50428-89-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
AB Bis(1-propynyl)methanol (I), bis(phenylethynyl)methanol (II), and tetrakis(1-propynyl)ethane-1,2-diol (III) are highly activated propargyl alcohols. Because of their sensitivity to acid, conversions of I and II to carbamate, ester, ether, and halide proceed best under neutral or basic conditions. Even so, disruptions of the diyne system are common, e.g., the formation of 4-bromo-2,5-heptadiyne and 2-bromo-2,3-heptadien-5-yne from I, thermal cleavage of III, and a base-catalyzed ynol to enone rearrangement of II to 1,5-diphenylpent-1-en-4-yn-3-one (IV). It is shown that the conversion of 1,3-diphenylpropynol (V) to 1,3-diphenylpropenone (VI) in the presence of base is another example of this rearrangement and that reactions which appear to be characteristic of the ynol (II, V) are probably those of the enone (IV, VI). The question of conjugation in skipped 1,4-diynes is discussed in the context of the uv spectra of several series and it is concluded that, in the diethynyl methanes, carbinols, and ketones, the central function at the 3 carbon does transmit conjugation. The trialkylethynylcarbinols are anomalous in that their uv absorption bands are decidedly hypsochromic relative to all members of the diethynyl families.

L9 ANSWER 3 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1964:19768 CAPLUS
DOCUMENT NUMBER: 60:19768
ORIGINAL REFERENCE NO.: 60:3495b-c
TITLE: Polarographic determination of 1,3,5-triphenyl-2-pyrazoline in plastic scintillators
AUTHOR(S): Belous, G. G.; Bezuglyi, V. D.
CORPORATE SOURCE: Sci. Res. Inst. Single Crystals, Scintillating Material, and Pure Chem. Substances, Kharkov
SOURCE: Zhurnal Analiticheskoi Khimii (1963), 18(10), 1250-4
CODEN: ZAKHA8; ISSN: 0044-4502
DOCUMENT TYPE: Journal

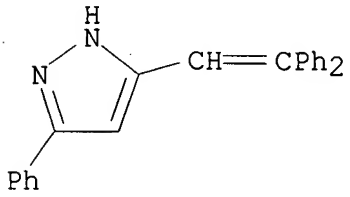
LANGUAGE: Unavailable
IT 2515-62-0, 2-Pyrazoline, 1,5-diphenyl-3-styryl-
(polarography of)
RN 2515-62-0 CAPLUS
CN 1H-Pyrazole, 4,5-dihydro-1,5-diphenyl-3-(2-phenylethenyl)- (CA INDEX NAME)



CC 2 (Analytical Chemistry)
IT 2515-59-5, 2-Pyrazoline, 5-(p-chlorophenyl)-1,3-diphenyl-
2515-62-0, 2-Pyrazoline, 1,5-diphenyl-3-styryl- 2574-33-6,
2-Pyrazoline, 5-(p-methoxyphenyl)-1,3-diphenyl- 7245-46-7,
2-Pyrazoline,
5-(o-chlorophenyl)-1,3-diphenyl-
(polarography of)
AB The polarographic behavior of the following 2-pyrazoline derivs., 1,3-diphenyl-5-(p-methoxyphenyl)-, 1,3diphenyl-5-(p-chlorophenyl)-, 1,3-phenyl-6-(o-chlorophenyl, 1,5diphenyl-5-styryl-, and 1,3,5-triphenyl-2-pyrazoline (I) in alc.aqueous buffer solns. and in neutral salt solns. was studied. In acid solns. the derivs. yield H catalytic waves which decrease with increasing pH and disappear at pH 7, and they yield diffusion waves in solns. of Et4N salts and bases in 92% alc. The mechanism of the electrode reduction of the derivs. is suggested. I does not form a wave in 0.1M LiCl, and in 0.1M LiOH it forms a diffusion wave which nearly blends with the background wave. For the determination of I in plastic scintillator. Dissolve 0.5 g. of polystyrene containing 0.1-1.5% of I in 5 cc. dioxane, and make up to 25 cc. with 5 X 10-2M (C2H5)4NI in 92% EtOH. Filter the precipitated polystyrene, and analyze 3 cc. of the filtrate polarographically, starting at -1.8 v. The error is ≤5%.

L9 ANSWER 4 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1961:124595 CAPLUS
DOCUMENT NUMBER: 55:124595
ORIGINAL REFERENCE NO.: 55:23420g-i,23421a-i,23422a-g
TITLE: Condensation of dialkali metal β-diketones with ketones or aldehydes to form hydroxy β-diketones. Dehydration products. Equilibrium factors
AUTHOR(S): Light, Robley J.; Hauser, Charles R.

CORPORATE SOURCE: Duke Univ., Durham, NC
SOURCE: Journal of Organic Chemistry (1961), 26, 1716-24
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 55:124595
IT 114537-74-5P, Pyrazole, 3(or 5)-(2,2-diphenylvinyl)-5(or 3)-phenyl-
RL: PREP (Preparation)
(preparation of)
RN 114537-74-5 CAPLUS
CN Pyrazole, 3(or 5)-(2,2-diphenylvinyl)-5(or 3)-phenyl- (6CI) (CA INDEX NAME)



CC 10E (Organic Chemistry: Benzene Derivatives)
IT 606-84-8P, Acrylic acid, 3,3-diphenyl- 4456-79-5P, Acryloyl chloride, 3,3-diphenyl- 5198-70-9P, 4H-Pyran-4-one, 2,3-dihydro-2-methyl-2,6-diphenyl- 6343-33-5P, 4-Pentene-1,3-dione, 1,5,5-triphenyl- 7248-82-0P, 2,4-Hexanedione, 6-(p-chlorophenyl)-6-hydroxy-6-phenyl-, copper derivative 7248-82-0P, 2,4-Hexanedione, 6-(p-chlorophenyl)-6-hydroxy-6-phenyl- 72610-55-0P, 1,3-Pentanedione, 5-hydroxy-1,5,5-triphenyl- 72610-56-1P, 1,3-Pentanedione, 5-hydroxy-5-(p-methoxyphenyl)-1-phenyl- 72610-56-1P, 1,3-Pentanedione, 5-hydroxy-5-(p-methoxyphenyl)-1-phenyl-, copper derivative 72610-62-9P, 2,4-Hexanedione, 6-hydroxy-6,6-diphenyl- 72610-62-9P, 2,4-Hexanedione, 6-hydroxy-6,6-diphenyl-, copper derivative 101723-58-4P, 4-Pentene-1,3-dione, 5-(p-methoxyphenyl)-1-phenyl- 102593-55-5P, 4H-Pyran-4-one, 2,3-dihydro-2,2,6-triphenyl- 109251-04-9P, 5-Hexene-2,4-dione, 6,6-diphenyl- 109253-80-7P, 4-Hexene-1,3-dione, 1,5-diphenyl 109253-88-5P, 4H-Pyran-4-one, 2,3-dihydro-6-methyl-2,2-diphenyl- 109393-85-3P, 1,3-Hexanedione, 5-hydroxy-1,5-diphenyl- 109393-85-3P, 1,3-Hexanedione, 5-hydroxy-1,5-diphenyl-, copper derivative 112115-94-3P, 1,3-Pentanedione, 5-(p-chlorophenyl)-5-hydroxy-1,5-diphenyl- 114537-74-5P, Pyrazole, 3(or 5)-(2,2-diphenylvinyl)-5(or 3)-phenyl- 116603-61-3P, Pyrazole-3(or 5)-ethanol, α,α,5(or α,α,3)-triphenyl- 127596-56-9P, 4-Pentene-1,3-dione, 1,5,5-triphenyl-, copper derivative 127596-57-0P, 1,3-Pentanedione, 5-(p-chlorophenyl)-5-hydroxy-1,5-diphenyl-, copper derivative 127596-58-1P,

1,3-Pentanedione, 5-hydroxy-1,5,5-triphenyl-, copper derivative
127688-06-6P, 4-Pentene-1,3-dione, 5-(p-methoxyphenyl)-1-phenyl-, copper
derivative 127794-95-0P, 5-Hexene-2,4-dione, 6,6-diphenyl-, copper derivative
127796-38-7P, 4-Hexene-1,3-dione, 1,5-diphenyl, copper derivative
RL: PREP (Preparation)
(preparation of)
AB The terminal carbanion of dipotassiobenzoylacetone (I) and
dipotassioacetylacetone (II) underwent addition reactions with the CO group
of certain ketones having no α-H to form the corresponding hydroxy
βdiones. While I apparently ionized the α-H of PhAc (III),
dilithiobenzoylacetone (IV) underwent addition with III and with
cyclohexanone (V) to form the hydroxy β-diones. Acid catalyzed
dehydrations of these compds. produced corresponding unsatd. β-diones
and, in certain cases, an isomeric product that appeared to be the
dihydropyrone. Certain of the dihydropyrones were converted to the
unsatd. β-diones with alc. KOH or MeOH-HCl and each
dehydration product yielded a mixture of the 2 isomers with cold H2SO4. A
hydroxy β-dione and its unsatd. β-dione were cyclized with N2H4
to the corresponding pyrazoles. The former pyrazole was dehydrated to
give the latter. A hydroxy β-dione underwent cleavage with KOCMe3 in
Me3COH to regenerate the ketone and β-dione. Equilibrium factors were
considered. Condensation of I. Solid benzoylacetone (Va) (16.2 g.) added
to 0.2 mole KNH2 in 300 ml. anhydrous NH3 then 50 ml. Et2O, the solution of I
stirred 0.5 hr., 0.1 mole ketone or aldehyde in 50 ml. Et2O added, the
mixture stirred 1 hr., poured into a liquid NH3 solution of 15 g. NH4Cl, the
mixture evaporated, and an Et2O suspension of the residue shaken with dilute HCl,
and evaporated gave a residue, which was recrystd. directly or first
triturated with hexane to give the solid hydroxy-β-diones. PhCO
condensed with Va with no Et2O gave only 18% hydroxy β-dione.
Method B. Condensations of II. Acetylacetone (Vb) (20 g.)
treated with liquid NH3, the NH4 salt added to 0.4 mole KNH2 in 500 ml.
liquid NH3, the suspension of II stirred 0.5 hr. then stirred 1 hr. with
36.4 g. Ph2CO, and the product worked up gave the hydroxy β-diones.
II (0.1 mole) in 300 ml. NH3 was prepared by use of one half the
usual amts. of reagents, 21.6 g. solid p-chlorobenzophenone (VI) added,
the mixture stirred 1 hr., neutralized, and worked up as above except that 2
procedures were compared for purification of the crude residue. Half
(13.15 g.) of the crude residue recrystd. from ligroine gave 6.7 g.
product. The other half treated with Cu(OAc)2 formed 14.6 g. crude Cu
chelate. This Cu chelate decomposed on shaking with Et2O and dilute HCl. The
Et2O layer washed and evaporated gave 8.2 g. product, which had two

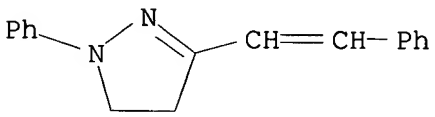
differently melting forms. Method C. Condensations of IV. Benzoylacetone (16.2 g.) in 50 ml. Et2O was added to 0.2 mole LiNH2 in 300 ml. NH3, the mixture stirred 45 min., and 0.1 mole ketone in Et2O added. The reaction mixture from III was stirred 1 hr. and the one with V 2 hrs., neutralized, and worked up as above. An alternative method for condensing benzoylacetone with III involved the addition of 12.7 g. dried LiCl and 25 ml. Et2O to 0.1 mole I in 300 ml. NH3. The mixture left 3 hrs. with 12 g. ketone and stirred 1 hr. gave 45% product. General procedure for Cu chelates. In procedure A, a filtered solution of 20-50 ml. Cu(OAc)2 was added to a MeOH solution (10-20 ml.) of the β-diketone (0.5-1.0 g.), the mixture cooled, and the chelate triturated with ligroine or MeOH. In procedure B, the Cu(OAc)2 was added in MeOH instead of H2O. In procedure C, an Et2O solution of the β-dione was stirred with a saturated aqueous solution of Cu(OAc)2 several hrs. and the chelate filtered off if insol. in Et2O, but obtained by evaporating the layer if soluble in Et2O. The following results were obtained (ketone or aldehyde, β-diketone, base, product, m.p., % yield, and m.p. of the Cu chelate given): anisaldehyde, Va, KNH2, 1-hydroxy-1-(p-methoxyphenyl)-5-phenyl-3,5-pentanedione (VII), 103-5°, 49, 185-7°; Ph2CO, Va, KNH2, 1-hydroxy-1,1,5-triphenyl-3,5-pentanedione (VIII), 115-16°, 73, 196-9°; VI, Va, KNH2, 1-(p-chlorophenyl)-1,5-diphenyl-1-hydroxy-3,5-pentanedione, 116-18°, 69, 194-6°; Ph2CO, Vb, KNH2, 1,1-diphenyl-1-hydroxy-3,5-hexanedione (IX), 133-5°, 73, 178-9.5°; VI, Vb, KNH2, 1-(p-chlorophenyl)-1-hydroxy-1-phenyl-3,5-hexanedione, 101-2.5° and 80-1.5°, 52, 161.5-3.0°; III, Va, LiNH2, 2,6-diphenyl-2-hydroxy-4,6-hexanedione (X), 85-7°, 40, 166-7.5°; V, Va, LiNH2, 1-hydroxy-1,1-pentamethylene-5-phenyl-3,5-pentanedione, 68-9°, 34, 207-9°. Dehydration of hydroxy β-diones. Method A, with MeOH-HCl. The hydroxy β-dione (2 g.) in 25 ml. MeOH and 3 ml. concentrated HCl was refluxed 1 hr. The mixts. from VII and VIII were cooled and those from IX and X were diluted with H2O and extracted with Et2O. The products were isolated and identified as follows. The product from VII was 96% p-methoxycinnamoylacetophenone, m. 129-30.5° (C6H6-alc.); Cu chelate m. 226-9° (dioxane-H2O). The product from VIII was 74% β-phenylcinnamoylacetophenone (XI), m. 96-8°; Cu chelate m.

MeOH containing 1 ml. concentrated HCl gave 0.6 g. XI. XIV (0.5 g.) in 10 ml. 95% alc. left 2 days at room temperature with 1 g. KOH in 10 ml. 95% alc. gave 80% XI. VIII (1 g.) treated with 40 ml. 5% alc. KOH gave 0.5 g. VIII and 0.15 g. Cu chelate of VIII. Neither dehydrated product was detected. XV (0.5 g.) similarly treated with alc.-KOH and the extract treated with Cu(OAc)2 gave 0.3 g. Cu chelate of XII. IX (1. g.) treated with alc. KOH under similar conditions gave 35% recovered IX and 9% of its Cu chelate. Neither dehyration product was detected. VIII (1 g.) in 30 ml. 95% alc. added to 10 drops 95% N2H4 and the mixture heated 1 hr. gave essentially quant. 3-(2,2-diphenyl-2-hydroxyethyl)phenylpyrazole (XVI), m. 182-4°. Treating 1 g. XI with N2H4 similarly gave 96% 3-(2,2-diphenylethenyl)-5-phenylpyrazole (XVII), m. 160-2° (MeOH-H2O). XVI (1 g.) refluxed 7 hrs. in 15 ml. MeOH containing 1 ml. concentrated HCl and left 60 hrs. at room temperature gave 0.2 g. XVII. VIII (4 g.) refluxed 2 hrs. with 0.013 mole KOCMe3 in Me3COH, the mixture distilled 1 hr., dilute acid added, the mixture extracted with Et2O, and the extracted evaporated gave 80% Va, m. 58-61° (MeOH). The neutral ether layer remaining after extraction with NaOH washed, dried, and evaporated gave 2.6 g. liquid residue. Chromatography on Al2O3 gave 68% Ph2CO, m. 49-50°. Similarly, 0.012 mole VIII cleaved with 0.0026 and 0.026 mole KOCMe3 gave 64 and 62% Va and 59 and 62%, resp., Ph2CO. In a blank experiment with no KOCMe3, 73% VIII was recovered. KNH2 (0.1 mole) in 300 ml. NH3 treated with 0.1 mole Va in 50 ml. Et2O then after 25 min. with 0.1 mole Ph2CO in Et2O gave after 6 hrs. 95% Va and 87% Ph2CO. Similarly, monolithiobenzoylacetone was prepared from 0.1 mole each Va and LiNH2 and Et2O and after 2 hrs. the mixture neutralized gave 95% Va.

L9 ANSWER 5 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER:	1960:118199 CAPLUS
DOCUMENT NUMBER:	54:118199
ORIGINAL REFERENCE NO.:	54:22582c-i,22583a
TITLE:	Action of phenylhydrazine on Mannich bases of furfurylideneacetone
AUTHOR(S):	Andrisano, Renato; Chierici, Luigi
CORPORATE SOURCE:	Univ. Parma, Italy
SOURCE:	Gazzetta Chimica Italiana (1959), 89, 888-96 CODEN: GCITA9; ISSN: 0016-5603
DOCUMENT TYPE:	Journal

LANGUAGE: Unavailable
IT 2387-04-4, 2-Pyrazoline, 1-phenyl-3-styryl-
(spectrum of)
RN 2387-04-4 CAPLUS
CN 2-Pyrazoline, 1-phenyl-3-styryl- (6CI, 7CI, 8CI) (CA INDEX NAME)

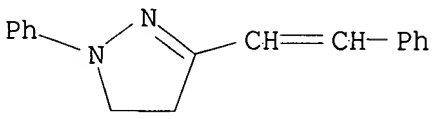


CC 10G (Organic Chemistry: Heterocyclic Compounds)
IT 623-15-4, 3-Buten-2-one, 4-(2-furyl)-
(Mannich bases from, reaction with phenylhydrazine)
IT 4747-46-0P, Pyrazole-3-carboxylic acid, 1-phenyl- 100969-09-3P,
2-Pyrazoline, 5-(2-furyl)-1-phenyl-3-vinyl- 100969-10-6P,
2-Pyrazoline,
3-[2-(2-furyl)vinyl]-1-phenyl- 101578-11-4P, 2-Pyrazoline,
3-(2-dimethylaminoethyl)-5-(2-furyl)-1-phenyl- 102129-21-5P,
2-Pyrazoline, 3-(2-diethylaminoethyl)-5-(2-furyl)-1-phenyl-,
hydrochloride
102129-27-1P, Morpholine, 4-[2-[5-(2-furyl)-1-phenyl-2-pyrazolin-3-
yl]ethyl]-, hydrochloride 102129-29-3P, Piperidine,
1-[2-[5-(2-furyl)-1-
phenyl-2-pyrazolin-3-yl]ethyl]-, hydrochloride 102149-30-4P,
2-Pyrazoline, 3-(2-dimethylaminoethyl)-5-(2-furyl)-1-phenyl-,
hydrochloride 103388-53-0P, Piperidine, 1-[2-[5-(2-furyl)-1-phenyl-2-
pyrazolin-3-yl]ethyl]- 103906-49-6P, Morpholine, 4-[2-[5-(2-furyl)-1-
phenyl-2-pyrazolin-3-yl]ethyl]- 110057-16-4P, Ammonium,
diethyl[2-[5-(2-furyl)-1-phenyl-2-pyrazolin-3-yl]ethyl]methyl-, iodide
110247-15-9P, 2-Pyrazoline,
3-(2-diethylaminoethyl)-5-(2-furyl)-1-phenyl-
117124-02-4P, 4-[2-[5-(2-Furyl)-1-phenyl-2-pyrazolin-3-yl]ethyl]-4-
methylmorpholinium iodide 117878-33-8P, Piperidinium,
1-[2-[5-(2-furyl)-1-phenyl-2-pyrazolin-3-yl]ethyl]-1-methyl-, iodide
RL: PREP (Preparation)
(preparation of)
IT 100-63-0, Hydrazine, phenyl-
(reaction with Mannich bases)
IT 2387-04-4, 2-Pyrazoline, 1-phenyl-3-styryl-
(spectrum of)
GI For diagram(s), see printed CA Issue.
AB cf. CA 54, 1211b. Aqueous 2-(C4H3O)CH:CHCO(CH2)2NR3 (I) (R = Me) (II)
HCl
salt heated 10 min. at 40° with 10% Na2CO3 and the oily product
extracted with Et2O and crystallized from Et2O with cooling gave
crystalline II, m.
31-2°. Similarly were produced the free bases I (R = Et)
(III), oil, I (NR3 = piperidino) (IV), oil, and I (NR2 = morpholino)
(V),

m. 78-9° (alc.). II (4.25 g.) in 20 ml. MeOH and 2.2 g. PhNHNH2 boiled 30 min. and cooled gave 2-(C4H3O)CH:CHC:N.NPh.CH2.CH2 (VI), m. 141° (MeOH), also given by similar treatment of IV and V and by a few min. boiling with III. III HCl salt (4 g. in 20 ml. alc.) boiled 30 min. with 1.5 g. PhNHNH2, the solution concentrated to 10 ml., cooled, and filtered, the precipitate extracted with Et2O from a small amount of insol. 2-(C4H3O)CH:CHC(:NNHPh)(CH2)2NEt2.HCl (VII), and the extract evaporated gave VI, with intensely yellow-green fluorescence in dilute Et2O, C6H6, or Me2CO solution, and giving a pos. reaction with Br vapor. The HCl salts of II and IV similarly gave VI with greater yields of the analogs of VII. KMnO4 (12.9 g.) in 650 ml. H2O at 60° shaken vigorously 4 hrs. with 2.4 g. VI, excess KMnO4 (12.9 g.) in 650 ml. H2O at 60° shaken vigorously 4 hrs. with 2.4 g. VI, excess KMnO4 reduced with HCHO, the mixture filtered and the MnO2 washed with hot H2O, the aqueous solution steam distilled 3-4 hrs., and the cooled distillate extracted with Et2O gave 1-phenylpyrazole-3-carboxylic acid, m. 142°, λ 264 mμ (log ε 4.17). VI reduced with Na and Na-Hg in alc. failed to liberate PhNH2, excluding the possibility of the formulation (C4H3O)CH:CHC(:NNHPh)CH:CH2. The structure of VI was confirmed by the preparation of the isomeric 2-(C4H3O)CH.CH2.C(CH:CH2):N.NPh (VIII). VII and the analogous phenylhydrazone HCl salts boiled in the appropriate acid media gave the corresponding pyrazolines, 2-(C4H3O)CH.CH2.C(CH2CH3NR2):N.NPh.HCl (IX), but with formation of larger amts. of VI than given by PhCH:CHC(:NNHPh)(CH2)2NR2.HCl (CA 53, 7145e). Aqueous IX (R = Et) boiled 10 min. with 10% Na2CO3 on a steam bath and the oily pyrazoline extracted with Et2O gave the corresponding crystalline base (X) of IX, m. 60° (absolute alc.). The analogous IX reacted similarly to give sufficiently pure X. X (0.01 mole) in 10 ml. MeOH refluxed 30 min. with excess MeI and the concentrated solution cooled gave X MeI salts (XI) [NR2 and m.p. (solvent) given]: NMe2, 202-3° (absolute alc.); NEt2, 199° (absolute alc.); piperidino, 198° (absolute alc.); morpholino, 197° (absolute alc.). XI (R = Et) (0.8 g.) refluxed 10 min. with excess NaOH and the oily pyrazoline crystallized from absolute alc. yielded VIII, m. 131°, similarly obtained from analogous XI, giving a pos. reaction with Br vapor and showing a weak violet fluorescence in dilute Et2O or C6H6 solns. VI, λ 263, 302, 385 mμ (log ε 4.00, 4.04, 4.56), showed a very similar spectrum to that of the analogous 1-phenyl-3-styryl-2-pyrazoline, λ 262, 318 mμ (log ε 4.19, 4.50), but differed from that of the isomeric VIII, λ 246, 337 mμ (log ε 4.03, 4.28). Thus, phenylhydrazones of Mannich

bases existed in stereoisomeric forms or the phenylhydrazone reacted under the conditions of the above cyclization procedure in 2 stereoisomeric modifications.

L9 ANSWER 6 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1960:62686 CAPLUS
DOCUMENT NUMBER: 54:62686
ORIGINAL REFERENCE NO.: 54:12116b-i
TITLE: Action of phenylhydrazine on Mannich bases from benzylideneacetone
AUTHOR(S): Andrisano, Renato; Chierici, Luigi
CORPORATE SOURCE: Univ. Parma
SOURCE: Gazzetta Chimica Italiana (1959), 89, 505-16
CODEN: GCITA9; ISSN: 0016-5603
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 54:62686
IT 2387-04-4P, 2-Pyrazoline, 1-phenyl-3-styryl-
RL: PREP (Preparation)
(preparation of)
RN 2387-04-4 CAPLUS
CN 2-Pyrazoline, 1-phenyl-3-styryl- (6CI, 7CI, 8CI) (CA INDEX NAME)

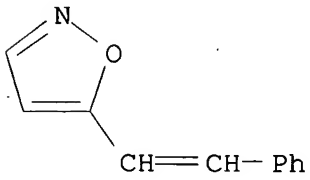


CC 10G (Organic Chemistry: Heterocyclic Compounds)
IT Mannich bases
(from 4-phenyl-3-buten-2-one, reaction with phenylhydrazine)
IT 122-57-6, 3-Buten-2-one, 4-phenyl-
(Mannich bases from, reaction with phenylhydrazine)
IT 2387-04-4P, 2-Pyrazoline, 1-phenyl-3-styryl- 63314-75-0P, Ammonium, [2-(1,5-diphenyl-2-pyrazolin-3-yl)ethyl]trimethyl-, iodide 63314-76-1P, 2-Pyrazoline, 1,5-diphenyl-3-vinyl- 90915-40-5P, 2-Pyrazoline-3-carboxylic acid, 1-phenyl- 110441-80-0P, 1-Penten-3-one, 5-dimethylamino-1-phenyl-, phenylhydrazone, hydrochloride 110441-81-1P, 2-Pyrazoline, 3-(2-dimethylaminoethyl)-1,5-diphenyl-, hydrochloride 112657-94-0P, Dibenzo[a,c]phenazine, 10-methyl- 114033-86-2P, Piperidine, 1-[2-(1,5-diphenyl-2-pyrazolin-3-yl)ethyl]-, hydrochloride 114063-26-2P, Ammonium, [2-(1,5-diphenyl-2-pyrazolin-3-yl)ethyl]diethylmethyl-, iodide 118927-75-6P, Piperidinium, 1-[2-(1,5-diphenyl-2-pyrazolin-3-yl)ethyl]-1-methyl-, iodide 122765-80-4P, 4-[2-(1,5-Diphenyl-2-pyrazolin-3-yl)ethyl]-4-methylmorpholinium iodide 132105-77-2P, Morpholine, 4-[2-(1,5-diphenyl-2-pyrazolin-3-yl)ethyl]-, hydrochloride 860447-35-4P, 2-Pyrazoline,

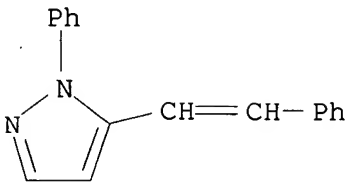
3-(2-diethylaminoethyl)-1,5-diphenyl-, hydrochloride
RL: PREP (Preparation)
(preparation of)
IT 100-63-0, Hydrazine, phenyl-
(reaction with Mannich bases)
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 53, 4185a. Treatment of Mannich base HCl salts, PhCH:CHCOCH2CH2NR2.HCl (I), with PhNHNH2 gave the corresponding phenylhydrazones (II), isomerized to the pyrazoline HCl salts, H2C.CHPh.NPh.N:CCH2CH2NR2.HCl (III), together with small amts. of 1-phenyl-3-styrylpyrazoline (IV). Addition of PhNHNH2 to the corresponding free Mannich base (V) gave almost exclusively IV, with traces of 1,5-diphenyl-3-vinylpyrazoline (VI), suggesting that II may act in one of two stereoisomeric forms according to the adopted conditions. PhCH:CHAc (14.6 g.), 12.5 g. morpholine-HCl, and 4.2 g. paraformaldehyde refluxed 5 min. in 10 ml. alc. and the product crystallized (alc.) gave I (R2 = CH2CH2 OCH2CH2) (VII), m. 155°. I (R = Me) (VIII) in H2O made alkaline with 10% Na2CO3 and heated 10 min. on steam bath, the oily base extracted with Et2O and the washed and dried extract evaporated, the base (3.2 g.) in 150 ml. MeOH heated 30 min. on a steam bath with 1.6 g. PhNHNH2, and the crystalline product recrystd. (MeOH) gave IV, m. 147°, pos. reaction with Br vapor, intense yellow-green fluorescence in dilute solution in Et2O, C6H6, or Me2CO, not liberating PhNH2 on reduction in absolute alc. with Na or Na-Hg. KMnO4 (6.5 g.) in 325 ml. boiling H2O stirred vigorously 2 hrs. with 1.2 g. IV and the excess KMnO4 reduced with HCHO, the filtered solution and aqueous washings acidified with H2SO4 and the solution freed from BzOH by steam distillation, extracted with Et2O, and the product repeatedly crystallized from H2O gave authentic 1-phenyl-3-pyrazolecarboxylic acid, m. 142°, λ 264 mμ (log ε 4.17). VII (11.3 g.) in alc. treated dropwise at 0° with 4.2 g. freshly distilled PhNNH2 in AcOH and the product recrystd. (alc.) gave II (R2 = CH2CH2OCH2CH2), m. 176°. II (2.5 g. similarly prepared from VII) in 30 ml. 1:5 AcOHH2O refluxed 30 min. and the solution concentrated on a steam bath, the concentrate diluted with 150 ml. Et2O and the precipitate, freed from traces of IV by extraction with Et2O gave III (R = Me) (IX), m. 176°. Similarly were prepared the corresponding III (R2 and m.p. given): Et2, 142-3°; (CH2)5, 197°; CH2CH2OCH2CH2, 172°. IX in H2O made alkaline with 10% Na2CO3 and heated 10 min. on a steam bath, the cooled solution extracted with Et2O and the washed and dried extract evaporated, the pyrazoline (3 g.) taken up in 10 ml. MeOH and refluxed 30 min. with MeI,

the cooled mixture filtered, and the precipitate recrystd. (alc.) gave H2C.CHPh.NPh.N:CCH2CH2NR2.MeI (X, R = Me) (XI), m. 202-3°. Similarly were prepared the corresponding X (R2 and m.p. given): Et2, 212°; (CH2)5, 202°; CH2CH2OCH2CH2, 201°. XI (1 g.) in MeOH refluxed 30 min. in 6 ml. 10% NaOH and the product recrystd. (absolute alc.) gave VI, m. 139-40°, similarly formed from X, with violet fluorescence in dilute solns. in Et2O, C6H6, and Me2CO, pos. reaction with Br vapor. The structure assigned to IV was further confirmed by ultraviolet absorption measurements in 0.001% alc. solns. (compound and λ in mμ (log ε) given): IV, 262, 381 (4.19, 4.50); VI, 248, 341 (3.98, 4.27); II (R = Me), 258, 361 (4.25, 4.49); PhCH:CHCH:NNHPh (Grammaticakis, C.A. 42, 531g), 254, 286.5, 368 (4.08, 3.96, 4.62).

L9 ANSWER 7 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1948:25374 CAPLUS
DOCUMENT NUMBER: 42:25374
ORIGINAL REFERENCE NO.: 42:5450f-i,5451a-i,5452a-i,5453a-d
TITLE: Heterocyclic syntheses. IX. Ketone reagents and anils of hydroxymethylene ketones
AUTHOR(S): Panizzi, Luigi; Monti, Elios
CORPORATE SOURCE: Ist. chim. generale anal. politec., Milan, Italy
SOURCE: Gazzetta Chimica Italiana (1947), 77, 556-71
CODEN: GCITA9; ISSN: 0016-5603
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
IT 91137-09-6P, Isoxazole, 5-styryl- 93323-27-4P, Pyrazole, 1-phenyl-5-styryl-
RL: PREP (Preparation)
(preparation of)
RN 91137-09-6 CAPLUS
CN Isoxazole, 5-(2-phenylethenyl)- (9CI) (CA INDEX NAME)



RN 93323-27-4 CAPLUS
CN Pyrazole, 1-phenyl-5-styryl- (7CI) (CA INDEX NAME)



CC 10 (Organic Chemistry)
IT Schiff bases
(of hydroxymethylene ketones)
IT 1006-67-3P, Isoxazole, 5-phenyl- 1133-77-3P, 5-Pyrazolecarboxylic acid,
1-phenyl- 1215-50-5P, Acrylophenone, 3-anilino- 2321-77-9P, Acetoacetonitrile, p-nitrophenylhydrazone 2515-61-9P, 2-Pyrazoline, 1,5-diphenyl- 5765-44-6P, Isoxazole, 5-methyl- 6704-83-2P, 4-Pentenenitrile, 3-oxo-5-phenyl- 6831-89-6P, Pyrazole, 1,5-diphenyl- 20362-54-3P, Thiazole, 2,2'-dithiobis- 36772-30-2P, 4(1H)-Pyridone, 2,3-dihydro-2,2-dimethyl-1-phenyl- 36772-31-3P, 4(1H)-Pyridone, 2,3-dihydro-2,2-dimethyl-1-phenyl-, oxime 40640-30-0P, Pyrazole, 1,5-diphenyl-4-phenylazo- 84637-25-2P, Acetonitrile, benzoyl-, p-nitrophenylhydrazone 91137-09-6P, Isoxazole, 5-styryl- 93323-27-4P, Pyrazole, 1-phenyl-5-styryl- 109448-37-5P, 3-Pentadienone, 1-anilino-5-phenyl- 111152-96-6P, Pyrazole, 5-methyl-1-phenyl-4-phenylazo- 854472-23-4P, 3-Buten-2-one, 4-anilino-3-(p-nitrophenylazo)- 855357-07-2P, 3-Pentadienone, 1-anilino-5-phenyl-2-phenylazo- 855357-08-3P, 3-Pentadienone, 1-anilino-2-(p-nitrophenylazo)-5-phenyl- 855443-75-3P, 4-Pentenenitrile,
3-oxo-5-phenyl-, p-nitrophenylhydrazone 856969-72-7P, 4(1H)-Pyridone, 2,3-dihydro-2,2-dimethyl-1-[p-(p-nitrophenylazo)phenyl]- 858814-02-5P,
3-Buten-2-one, 4-anilino-3-phenylazo- 858822-46-5P, Acrylophenone, 3-anilino-2-phenylazo- 858822-49-8P, Acrylophenone, 3-anilino-2-(p-nitrophenylazo)-
RL: PREP (Preparation)
(preparation of)
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 42, 903h. Whereas NH2OH.HCl (I) and PhNHNH2 (II) react with both
the CO and the CHOH group of RCOCH:CHOH compds., and form 3- and 5-substituted isoxazoles and pyrazoles, with RCOCH:CHOR' (III) compds. the
reaction is confined to the CO group, whereby only 3-substituted heterocyclic derivs. are formed (cf. P. and Sbrillo-Siena, C.A. 41, 1221d). The present work describes a method for prepg
. exclusively the corresponding 5 substituted derivs., viz., by making I
and II react with RCOCH:CHNHPh (IV) compds. In each case PhNH2 (V) and water are evolved, and cyclization then takes place. The IV structure is

preferred to the RCOCH2CH:NPh (VI) structure because it is in better accord with the notable stability to heat, acids, and alkalies, with the formation of similar compds. from secondary anilines, and with spectrochem. measurements of analogous imino-enol-amine systems. However, if the compds. react also in the VI form, the mechanism is probably: A comparison of this reaction with that of III compds., in which tautomerism is impossible, indicates that the presence in IV of the N and of a mobile amino-H has a decisive role in the course of the reaction. The problem should be resolved by the behavior of ketone derivs. formed from hydroxymethylene ketones and secondary amines, where again tautomerism would be impossible. HCO2Et (22 g.) and 14.5 g. acetone, added slowly to a suspension of 5.7 g. powdered Na in 120 cc. anhydrous C6H6, allowed to stand several hrs. at 30-40°, agitated with ice-water, the aqueous layer treated with excess V in AcOH, the orange-brown oil which seps. extracted with C6H6, the extract dried by CaCl2, evaporated, and distilled in vacuo, and the fraction (13 g.) which b12 148-50° allowed to solidify, washed with ligroin, and purified by C6H6-ligroin, yields acetylacetaldehyde anil, AcCH:CHNHPh (VII), m. 50-2°; FeCl3 turns its alc. solns. red. Alc.VII (1 g. in 5 cc.) and 0.65 g. I in a min. of water, refluxed 1.5 hrs., diluted with water, acidified (Congo red) with HCl, extracted with Et2O, the extract distilled, the fraction at 50° agitated with saturated aqueous CdCl2, and the addition product washed with EtOH and Et2O, dried, and distilled twice, yield 0.3 g. of 5-methylisoxazole (VIII). VIII (0.24 g.) and EtONa (from 0.1 g. Na and 1.5 cc. anhydrous EtOH), allowed to stand, diluted with water, 0.55 g. p-O2NC6H4NHNH2 (IX) in 3 cc. glacial AcOH added, then NaCl, allowed to stand 1 hr., filtered, and washed with water, yield p-O2NC6H4NHN:CMeCH2CN, m. 183-5° (cf. Justoni, C.A. 35, 5110.8). VII (1 g.), 0.71 g. II, 0.65 cc. concentrated HCl, and 10 cc. EtOH, refluxed 3 hrs., diluted with water, acidified (Congo red) with HCl, extracted with Et2O, the extract evaporated, the residue steam-distilled, the oil distillate extracted with Et2O, and the extract dried by Na2SO4 and distilled, leave a residue of PhN.N:CH.CH:CMe. Its chloroplatinate m. 193-6° (decomposition) (cf. Ber. 32, 2891(1899); Stoermer, C.A. 1, 1287), and its picrate m. 93-7° (cf. Ber. 32, 2891(1899); Stoermer, loc. cit.). Alc

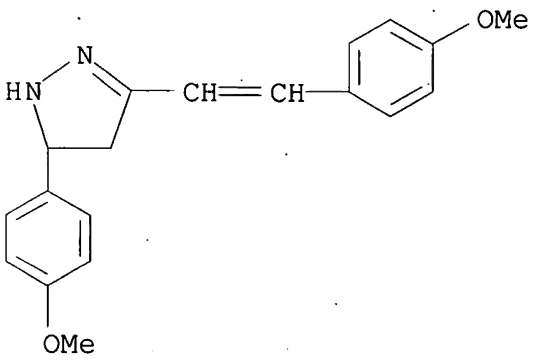
. VII (0.5 g. in 10 cc.), 1 g. NaOAc, and p-O2NC6H4N2Cl (X) (from 0.5 g.
IX), allowed to stand, and the precipitate purified by BuOH, yield (p-nitrophenylazo)acetylacetaldehyde anil, AcC(:CHNHPh)N:NC6H4NO2-p (XI), orange, m. 186-8° (decomposition); NaOH turns its alc. solns. intense red. An alc. suspension of XI (1 g. in 110 cc.) and 0.26 g. I, refluxed 3 hrs., allowed to stand, and the precipitate purified by BuOH, yield (p-nitrophenylazo)acetylacetaldehyde oxime, p-O2NC6H4N:NCHAcC(:NOH)H, orange-red, m. 221-3° (decomposition). Alc. VII (1 g. in 15 cc.), 1.8 g. NaOAc, and PhN2Cl (from 0.6 g. V), allowed to stand and the precipitate purified by EtOH, yield (phenylazo)acetylacetaldehyde anil (XII), yellow, m. 128-30°. XII (0.5 g.), 15 cc. glacial AcOH, and 0.2 g. II, heated 1.5 hrs. on a steam bath and allowed to stand, precipitate the hydrazone, AcCH(N:NPh)CH:NNHPh, golden yellow, m. 215-18°. The mother liquor, diluted, allowed to stand, and the precipitate purified by MeOH, yields PhN.CH:CH.C(N:NPh):CMe, m. 108-11°. PhAc (24 g.) and 14 g. HCO2Me, added slowly to a suspension of 5 g. powdered Na in 100 cc. anhydrous C6H6 (the reaction is energetic and must be cooled), allowed to stand, ice water added, a small excess of V.AcOH added to the aqueous layer, and the precipitate purified by BuOH, yields 36 g. BzCH:CHNHPh (XIII), lemon-yellow, m. 140-1° (cf. Claisen and Fischer, Ber. 21, 1137(1888)). Alc. XIII (4 g. in 20 cc.) and 1.9 g. I in a min. of water, heated 1 hr. at 100°, most of the EtOH evaporated, diluted with water, acidified (Congo red) with HCl, extracted with Et2O, the extract dried by Na2SO4, evaporated, and the residue (2.5 g.) fractionally distilled, yield 5-phenylisoxazole (XIV), b3-4 110° (cf. Claisen, Ber. 36, 3671(1909)). XIV (0.496 g.) and EtONa (from 0.35 g. Na and 5 cc. anhydrous EtOH), heated a short time at 40-50°, excess IX in AcOH added, allowed to stand overnight, and the precipitate washed and purified by BuOH, yield α-cyanoacetophenone p-nitrophenylhydrazone, p-O2NC6H4NHN:CPhCH2CN, yellow, m. 177-8°. XIII (3 g.), 1.74 g. II, 1.5 cc. concentrated HCl, and 40 cc. EtOH, refluxed 2 hrs., most of the EtOH evaporated, diluted with water, acidified with HCl (Congo red), extracted with Et2O, the extract evaporated, and the oil (2.6 g.) purified by distillation in vacuo, yield PhN.N:CH.CH:CPh (cf. Claisen and Fischer, loc. cit.). Reduction by Na and EtOH yields PhN.N:CH.CH2.CHPh, m. 133-5° (cf. Ber. 26, 112(1893)). XIII (3 g. in 300 cc. MeOH), excess NaOAc, and X (from 1.9 g.

p-O2NC6H4NH2), allowed to stand, and the precipitate purified by BuOH, yield (p-nitrophenylazo)benzoylacetaldehyde anil (XV), orange-red, m. 202-3°. XV (0.46 g.) and 0.1 g. I in 50 cc. EtOH, refluxed 1.5 hrs., evaporated, diluted with water, and the precipitate purified by BuOH, yield (p-nitrophenylazo)benzoylacetaldehyde oxime, m. 209-12°. Alkalies turn its alc. solns. orange-red. XIII (1 g.) in 150 cc. MeOH, 1.5 g. NaOAc, and PhN2Cl (from 0.5 g. V), allowed to stand, and the precipitate (0.3 g.) purified by EtOH, yield (phenylazo)benzoylacetaldehyde anil (XVI), orange-yellow, m. 137-9°. XVI (0.22 g.), 0.07 g. II, and 15 cc. glacial AcOH, heated 2 hrs. at 100°, diluted with water, partially neutralized, and the precipitate (0.17 g.) purified by EtOH, yield 1,5-diphenyl-4-phenylazopyrazole, PhN.CH:CH.C(N:NPh):CPh, yellow, m. 117-18°. PhCH:CHAc (7.3 g.), 4 g. HCO2Me, and a suspension of 1.25 g. powdered Na in 60 cc. anhydrous C6H6 react energetically and the mixture must be cooled; the product, allowed to stand, agitated with ice-water, excess V.AcOH added to the aqueous layer, and the precipitate purified by EtOH, yield approx. 20% of cinnamoylacetaldehyde anil, PhCH:CHCOCH:CHNHPh (XVII), yellow, m. 150-1°. XVII (2 g.) and 0.8 g. I in 25 cc. EtOH, refluxed 2 hrs., concentrated to a small volume, diluted with water, acidified (Congo red) with HCl, extracted with Et2O, the extract evaporated, the residue steam-distilled, the distillate allowed to solidify, and purified by petr. ether, yield 5-styrylisoxazole, O.N:CH.CH:CCH:CHPh (XVIII), m. 42-3°; its acetone solution decolorizes KMnO4; its AcOH solution decolorizes Br slowly. By treatment with cold EtONa solution, dilution with water, acidification, and purification by CCl4, XVIII forms cinnamoylacetonitrile, PhCH:CHCOCH2CN, m. 95-8°. With excess IX in AcOH, it ppts. the p-nitrophenylhydrazone, m. 210-12° (cf. Musante, C.A. 37, 2737.5). XVIII (2 g.), 0.95 g. II, 0.85 cc. concentrated HCl, and 15 cc. EtOH, refluxed 2 hrs., concentrated to a small volume, diluted with water, extracted with Et2O, the extract evaporated, the residue distilled in vacuo, and the distillate, b15-20 230°, allowed to solidify and purified by EtOH, yield 1-phenyl-5-styrylpyrazole (XIX), m. 127°, soluble in aqueous HCl. (NH4)2Cr2O7 (1.5 g.), added slowly to 0.8 g. XIX in 20 cc. boiling 20% H2SO4, extracted with Et2O, the extract evaporated, the residue taken up in aqueous Na2CO3, extracted with Et2O, the aqueous residue acidified with HCl, extracted with Et2O, the extract evaporated, and the residue heated at 110° (to remove

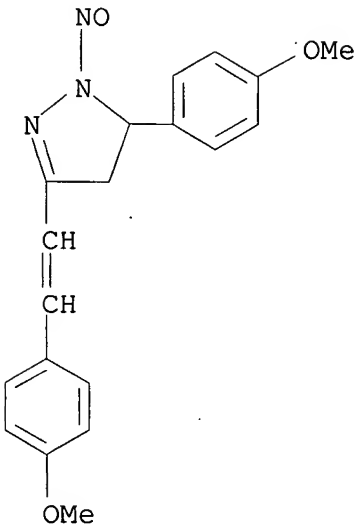
BzOH) and purified by boiling water, yields 0.2 g. 1-phenyl-5-pyrazolecarboxylic acid, PhN.N:CH.CH:CCO2H, m. 179-81°. X (from 0.3 g. p-O2NC6H4NH2), added to 0.5 g. XVII in 50 cc. MeOH and 1 g. NaOAc, and the precipitate (0.5 g.) purified by BuOH, yields (p-nitrophenylazo)cinnamoylacetaldehyde anil (XX), orange, m. 161-3°. XX (0.4 g.) in 50 cc. EtOH and 0.1 g. I, refluxed 2 hrs., concentrated to a small volume, and the residue allowed to solidify and purified by BuOH, yield (p-nitrophenylazo)cinnamoylacetaldehyde oxime, PhCH:CHCOCH(N:NC6H4NO2-p)C(:NOH)H, yellow, m. 194°. XVII (1 g.), 1.2 g. NaOAc, and PhN2Cl (from 0.4 g. V) in 100 cc. MeOH, allowed to stand 1 hr., and the precipitate purified by BuOH, yield (phenylazo)cinnamoylacetaldehyde anil (XXI), red, m. 148-9°. Alc. XXI (0.25 g. in 50 cc.), 0.1 g. II, and 0.1 cc. concentrated HCl, boiled a short time, allowed to stand, and the precipitate purified by BuOH, yield the phenylhydrazone, C23H20ON4, orange-yellow, m. 215-16°. When heated cautiously in vacuo, and the distillate purified by EtOH, it yields 1-phenyl-4-phenylazo-5-styrylpyrazole, yellow, m. 158-60°; a trace turns concentrated H2SO4 intense cherry-red. To study IV compds. in which R is Me2C:CH-, Me2C:CHCOCH2CHO (XXII) was made to react with V.AcOH with the intention of obtaining Me2C:CHCOCH:CHNHPh. However, the reaction was different and an isomer was obtained. Me2C:CHAc (20 g.), 16 g. HCO2Me, 100 cc. anhydrous C6H6, and MeONa (from 4.9 g. Na), kept below 10° overnight, agitated with ice-water, the aqueous layer treated with V.AcOH, the brown-red oil extracted with C6H6, the extract evaporated, the residue distilled in vacuo, the orange-red fraction, which b14 150-200°, allowed to partially solidify, filtered, and washed with ligroin, and the residue (6.5 g.), purified by CCl4, yields 1-phenyl-2,3-dehydro-6,6-dimethyl-4-piperidone, HC:CH.CO.CH2.CMe2.NPh (XXIII), m. 132°, soluble in dilute HCl (repptd. unaltered by alkalies); its CS2, solution absorbs Br; it does not immediately decolorize KMnO4 in acetone. XXIII (0.5 g.) in 5 cc. MeOH and 0.26 g. I, refluxed 3 hrs., diluted with water, extracted with Et2O, the aqueous layer made alkaline with NaOH, and the green-yellow precipitate (0.3 g.) purified by animal charcoal and ligroin, yield the oxime, HC:CH.C(:NOH).CH2.CMe2.NPh, m. 167-9°, soluble in dilute HCl (repptd. by alkalies). XXIII (0.5 g.), 1 g. NaOAc, and p-O2NC6H4N2Cl (from 0.35 g. p-O2NC6H4NH2) give 0.5 g. of a precipitate which, purified by EtOH, yields the p-nitrophenylazo derivative, HC:CH.CO.CH2.CMe2.NC6H4N:NC6H4NO2-p (XXIV),

carmine-red, m. 170°; its alc. solns. turn orange-red with NaOH. The constitution of XXIV seems, in view of the similarity between XXIII and dialkylanilines, more probable than that of a derivative formed by coupling on the piperidone nucleus.

L9 ANSWER 8 OF 8 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1948:13722 CAPLUS
DOCUMENT NUMBER: 42:13722
ORIGINAL REFERENCE NO.: 42:2967a-f
TITLE: Action of hydrazine hydrate on dianisylideneacetone and the decomposition of the pyrazoline base from them into a cyclopropane derivative
AUTHOR(S): Ushakov, M. I.; Shusherina, N. P.; Chinaeva, A. D.
SOURCE: Zhurnal Obshchei Khimii (1947), 17, 1678-83
CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE: Journal
LANGUAGE: Russian
IT 857219-17-1, 2-Pyrazoline, 5-(p-methoxyphenyl)-3-(p-methoxystyryl)- (and derivs.)
RN 857219-17-1 CAPLUS
CN 2-Pyrazoline, 5-(p-methoxyphenyl)-3-(p-methoxystyryl)- (5CI) (CA INDEX NAME)



IT 857219-23-9P, 2-Pyrazoline, 5-(p-methoxyphenyl)-3-(p-methoxystyryl)-1-nitroso-
RL: PREP (Preparation)
(preparation of)
RN 857219-23-9 CAPLUS
CN 2-Pyrazoline, 5-(p-methoxyphenyl)-3-(p-methoxystyryl)-1-nitroso- (5CI) (CA INDEX NAME)



CC 10 (Organic Chemistry)
IT 857219-17-1, 2-Pyrazoline, 5-(p-methoxyphenyl)-3-(p-methoxystyryl)-
(and derivs.)
IT 857219-23-9P, 2-Pyrazoline, 5-(p-methoxyphenyl)-3-(p-
methoxystyryl)-1-nitroso- 858422-82-9P, Cyclopropane,
1-(p-methoxyphenyl)-2-(p-methoxystyryl)- 858422-84-1P, Cyclopropane,
1-(p-methoxyphenethyl)-2-(p-methoxyphenyl)-
RL: PREP (Preparation)
(preparation of)
AB Dianisylideneacetone, (p-MeOC6H4CH:CH)2CO (5 g.), 50 cc. EtOH, and 3.24 g.
78% N2H4.H2O agitated 40 min. at 65-70° gave, on cooling, 67% of a pyrazoline derivative, C19H20O2N2, m. 130-1° (from EtOH); Ag salt, white crystals, darkening in the air or on heating (excess alc. leads to separation of metallic Ag); HCl salt, decompose 173-4° (from EtOH); nitroso derivative, m. 142° (from EtOH). When 16 g. pyrazoline derivative was heated at 15-16 mm. to 140°, N evolution began and was finally completed after 2 hrs. at 200-30°; the product in Et2O was treated with HCl to remove traces of the unreacted base and the residue on distillation gave 9 g. greenish oil, b3 189-90°, solidifying on standing, m. 44-5° (from EtOH), d450 1.0813, nD50 1.5676; the material decolorizes KMnO4 in CHCl3, gives with Br a green color turning to violet; on the basis of MR calcns. and chemical behavior the product is given the structure of 1-(p-methoxyphenyl)-2-[2-(p-methoxyphenyl)cyclopropyl]ethylene (I). With KMnO4 in dilute Me2CO it gave anisic acid and a solid, m. 112-13° (from EtOAc). Hydrogenation in EtOH over Pt black gave a product (II), C19H22O2, m. 70-1° (from EtOH), assigned the structure of the ethane analog of I. II (0.5 g.), 2.5 g. pyridine, and 0.5 g. Na heated 4 hrs. to 170-90° in a N atmospheric,

cooled, treated with pyridine, then with pyridine-H2O, extracted with Et2O,
and the aqueous solution acidified with 20% H2SO4 and extracted with Et2O gave 66%
1-(p-hydroxyphenyl)-2-[2-(p-hydroxyphenyl)cyclopropyl]ethane, m. 172-3° (from benzene); this (0.1 g.) in 2.5 cc. pyridine with 2.5 g. Ac2O yielded, after standing 2 days, the di-Ac derivative, m. 121-2° (from MeOH). The formation of the cyclopropane derivative is explained by an
intermediate RCH:CHCHCH2CHR, with an allylic system which can shift its double bond to give RCHCH:CHCH2CHR; the former structure can yield the cyclopropyl derivative on cyclization, as was the case in this instance, while
the 2nd form gives rise to a 5-membered ring, as with the Kizhner compound
(C.A. 10, 1338).

=> log y

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